

DEVELOPMENT OF SELF-DETOXIFYING MATERIALS FOR CHEMICAL PROTECTIVE CLOTHING

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ABSTRACT

The U.S. Army Natick Soldier Center has been developing methods to incorporate reactive compounds into chemical protective fabrics to decontaminate G-type agents, VX, and mustard (HD). These reactive compounds include: polyoxometalates, magnesium oxide and modified cyclodextrins. Polyoxometalates (POMs), prepared at Emory University, have been incorporated into activated carbon for use in carbon based fabrics and have also been combined with metal oxide powders and reacted with half mustard, CEES. Catalytic activity of the POM/Carbon, POM/MgO, POM/Al₂O₃, and POM alone in solution were compared to activities in organic fibers and films. Substituted cyclodextrins that were reported in 1992 to be scavengers and catalysts for the hydrolytic cleavage of the P-F bond in soman were used in this study. We report on the preparation and reactivity of a catalytic derivative of β -cyclodextrin (2-O-(4-carboxy-3-iodosobenzoyl)- β -cyclodextrin [IBA- β CD]) on fibers and films reacted against soman and the soman simulant, dimebu.

INTRODUCTION

Heteropoly compounds have been used extensively as unsupported solid acid catalysts in such processes as: 1) Friedal-Crafts alkylation and acetylation¹, 2) esterification and hydrolysis², and 3) selective oxidation of alkanes³. Polyoxometalates (a heteropoly acid of the type H₅PV₂Mo₁₀O₄₀) supported on porous carbons were reported to form selective and recoverable heterogeneous catalysts for the rapid room temperature oxidation of thioether analogues for mustard (HD)⁴. Nano size metal oxides have been reported to decontaminate chemical warfare agents^{5,6} and can exhibit biocidal activity toward spores of biological warfare (BW) analogues⁷. An iodosobenzoate derivative of β -cyclodextrin (IBA- β CD) was reported to catalyze the hydrolysis of soman and soman analogues^{8,9}. In this report we will focus on the reactivity of these catalysts on CW agent analogues when the catalysts are incorporated into porous carbon, organic fibers and film coatings for fabrics.

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SAMPLE PREPARATION

Polyoxometalates (POM) of the type $H_5PV_2Mo_{10}O_{40}$ were prepared at Emory University by Hill et al.⁴ The following activated carbons were used in the adsorption experiments with the POMs: Ambersorb (Rohm& Haas), Calgon (Calgon Corp.), and Maxsorb (Kansai Coke & Chemical). The carbons were reacted with the POM dissolved in either acetonitrile or tetrahydofuran in a molar ratio of 140:1 (Carbon:POM). The carbons were added to a stirred solution of the POM and reacted overnight at room temperature. The reacted carbons were filtered and the washings (10X) were analyzed by spectrophotometry (310nm) to estimate the extent of POM adsorbed. The amounts of POM adsorbed onto the carbons were in the range of 12-15%. Nano metal oxides were obtained from NanoScale, Inc., (Manhattan,KS). Both nano magnesium oxide and nano aluminum oxide were used in the study. The diameter of the nano particles ranged from 3-6 nm (data supplied by NanoScale, Inc.). The method incorporation of the POM into the nano metal oxides was the same as in the carbon reaction. And the amount of POM adsorbed by the metal oxides was 20%. IBA- β CD was synthesized by the method of Seltzman and Szulc shown in figure 1.⁸

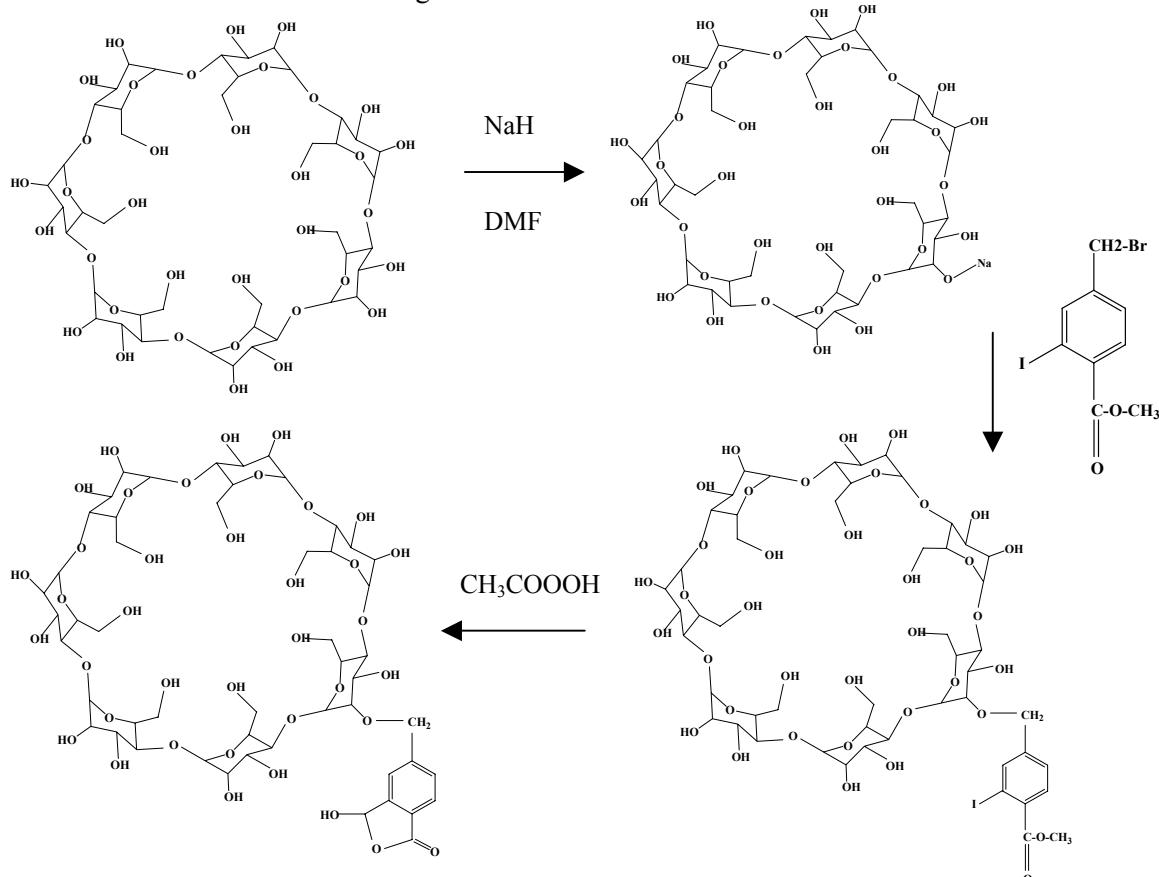


Figure 1. Synthetic preparation of substituted IBA- β CD (from reference 8).

Catalytic materials were incorporated into a 10% solution of polyurethane (either Estane® supplied by Noveon, Inc., or Pellethane®, supplied by Dow Chemical) in tetrahydrofuran (THF) and electrospun into microfibers after the method of Schreuder-Gibson et al.¹⁰ In figure 2 is shown a scanning electron micrograph of the electrospun polyurethane Pellethane® with typical fiber diameters ranging from 100-500 nm.

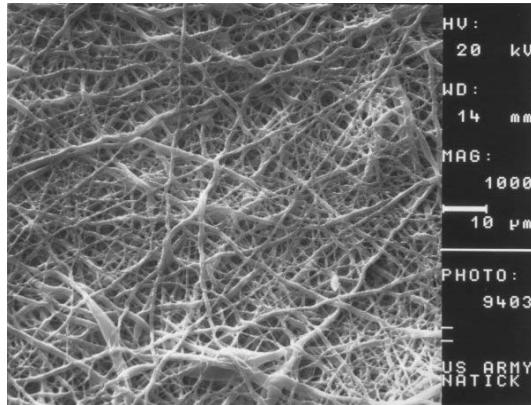


Figure 2. Electrospun fiber mat for encapsulating CW agent catalysts.

TESTING METHODS

The analysis of the reactivity of HD simulants against POM loaded carbons, POM loaded nano metal oxide particles, or electrospun microfiber mats with POM was performed in acetonitrile solutions containing 5×10^{-4} M concentration of chloroethyl ethylsulfide (CEES) and monitored using GC/MS with a H/P 1701 column (30mx0.53mm i.d.x 1 μ m film thickness). Catalytic hydrolysis of soman and soman simulants by IBA- β CD was monitored by the release of fluoride ion using a fluoride sensitive electrode (Orion Inc, Beverly, MA), by the method of Hoskin¹¹. The rate of hydrolysis is measured as μ moles of soman or soman simulant hydrolyzed per minute per milligram of IBA- β CD. We report this rate as Units/mg IBA- β CD. ESR spectra were measured with a Bruker X-Band spectrometer, Model 300. Spectra were measured with a 100 KHz magnetic field modulation, at a microwave power of 2mW. The modulation amplitude was 0.5-2.0G.

RESULTS

In Figure 3 are the results of multiple tests for a POM/Maxsorb heterogeneous supported catalyst incorporated in a polyurethane matrix, reacting on the HD analogue tetrahydrothiophene (THT) according to the reaction in equation 1.

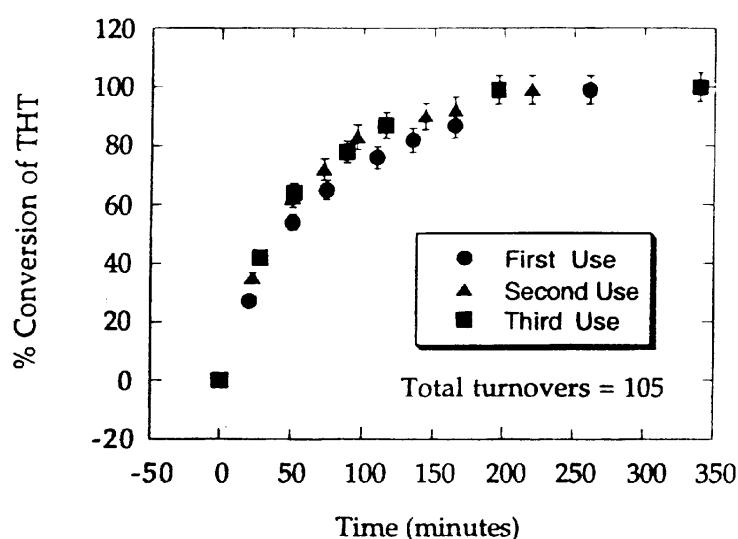
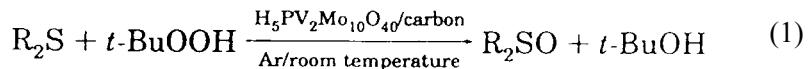


Figure 3. Reusability of POM in carbon fabric.



The catalytic action of POM is to form the sulfoxide exclusively as shown in equation 1. In the sulfoxide form, HD has been reported not to contribute to blistering pathology¹². Shown in figure 3, there appears to be no loss of catalytic activity in successive cycles for these supported catalyst compounds with the THT substrate, and 105 turnovers are observed for this compound.

Following the THT conversion study, reaction rates of adsorbed and fiber-encapsulated POM were measured for oxidative decomposition of CEES. In Figure 4 a comparison of POM encapsulated in microfibers and films with POM/Carbon, POM/ruthenium chloride and POM free in solution is shown.

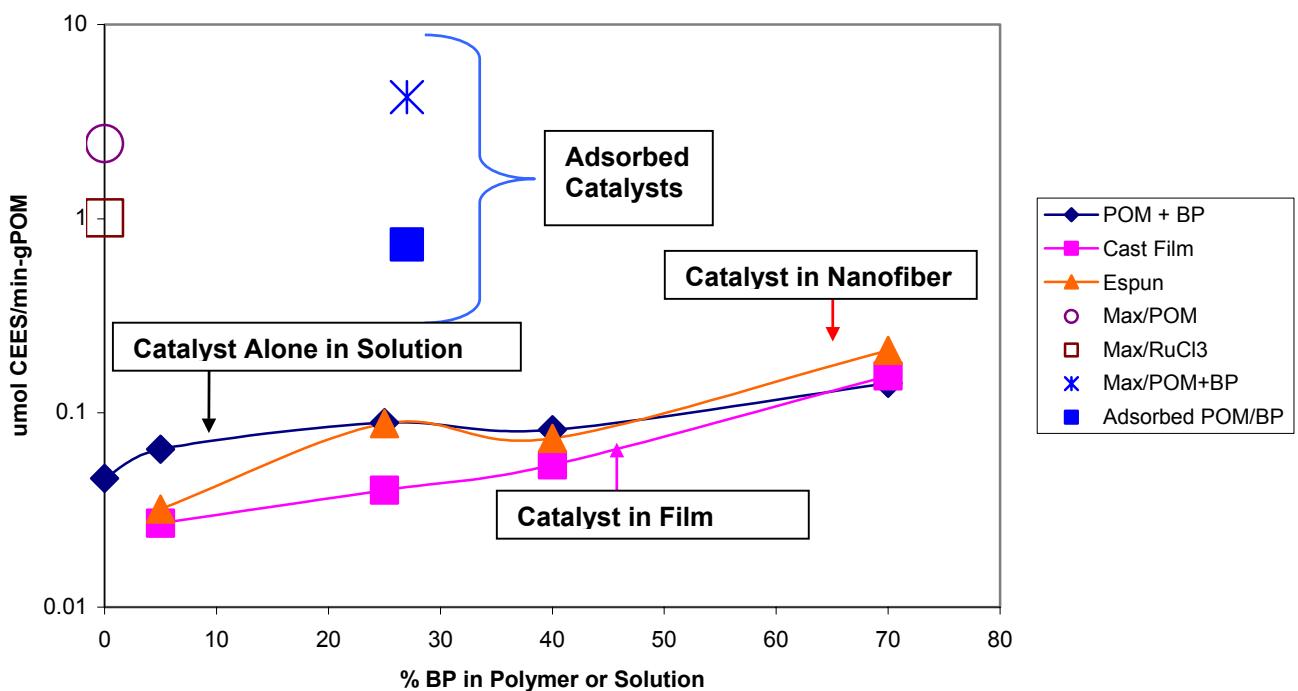


Figure 4. Comparison of CEES depletion rates at varied benzoyl peroxide concentrations for POM encapsulated in Pellethane® microfiber or film, adsorbed on carbon and free in solution.

Also shown is the effect of benzoyl peroxide (BP) on the reactivity of the system. Peroxides have been used as co-oxidants with POM to complete the catalytic cycle, re-oxidizing the spent polyoxometalate after reaction with CEES. For POM alone in solution, increasing levels of added BP increase the specific reaction rate of POM against CEES. This effect is also observed with POM and BP incorporated into electrospun fibers and into fabric coatings, and we see that at high BP levels within the fibers films, POM in the electrospun fibers oxidizes CEES at a higher specific rate than alone in solution. Figure 4 shows that the highest reaction rates were achieved for adsorbed POM. We compared adsorbed catalysts, Max/POM and Max/RuCl₃ (this sample was prepared from a solution of ruthenium chloride adsorbed on Maxsorb in the manner of the POM adsorption) without added BP in the reaction solution, and found that POM performed better than RuCl₃. Adsorbed Max/POM + BP was a measurement with BP added to the reaction solution; this condition was only slightly better than the reaction of Max/POM

with no added benzoyl peroxide in solution. An alternative method of incorporating the co-oxidant was examined by adsorbing BP from a solution in THF onto Max/POM, resulting in Max/POM/BP. This method of introducing BP into the reaction appeared to interfere with the POM reaction with CEES. It appears that a co-oxidant for the catalytic turnover of POM is not required when POM is adsorbed onto activated carbon. The reason for this observation is not known, and TEM studies to elucidate the position of POM within the micropores of Maxsorb were inconclusive.

In an effort to determine whether a re-oxidation cycle could be achieved between metal oxide surfaces and adsorbed POM, we examined the oxidative decomposition of CEES by POM/nano MgO and POM/nano Al_2O_3 and POM/micron Al_2O_3 . Seen in Figure 5, the effect of POM/nano MgO is compared with nano MgO alone, POM alone, and POM/ micron MgO in a solution oxidation of CEES with added benzoyl peroxide.

REACTION OF CEES with POM & POM/MgO

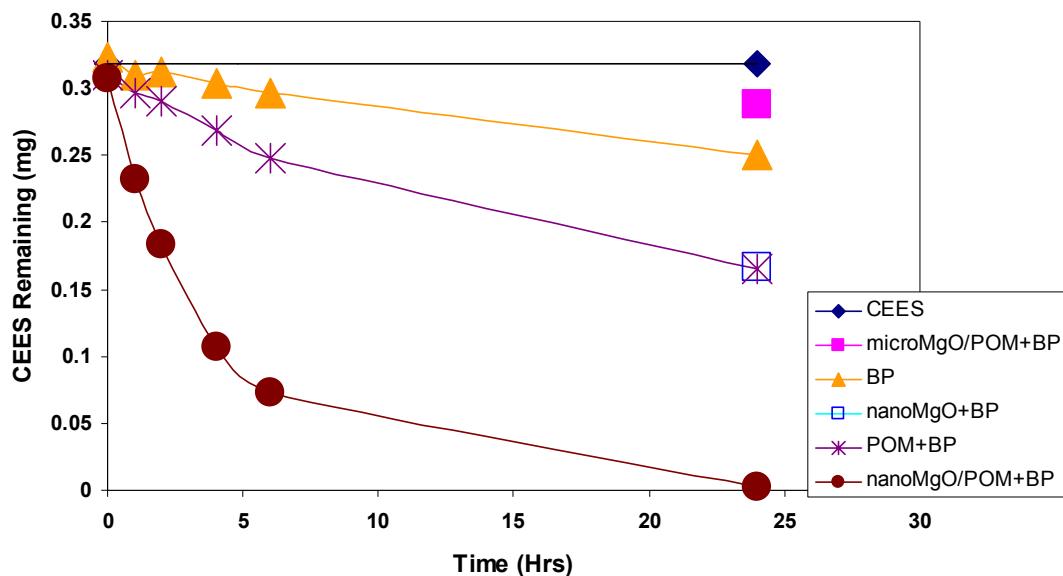


Figure 5. Reaction of micro MgO/POM, nano MgO/POM, nano MgO with CEES.

In Figure 5 it can be seen that when POM is incorporated into nano MgO there is an enhancement of reactivity towards CEES that is greater than the effect of either nano MgO and POM alone. This reaction enhancement is not realized when POM is adsorbed onto micron MgO. In order to determine the chemical differences of the surface adsorbed POM onto micron vs the nano MgO, ESR spectra for nano MgO/POM and micron MgO/POM were examined. Figure 6 shows significant spectral differences in these samples.

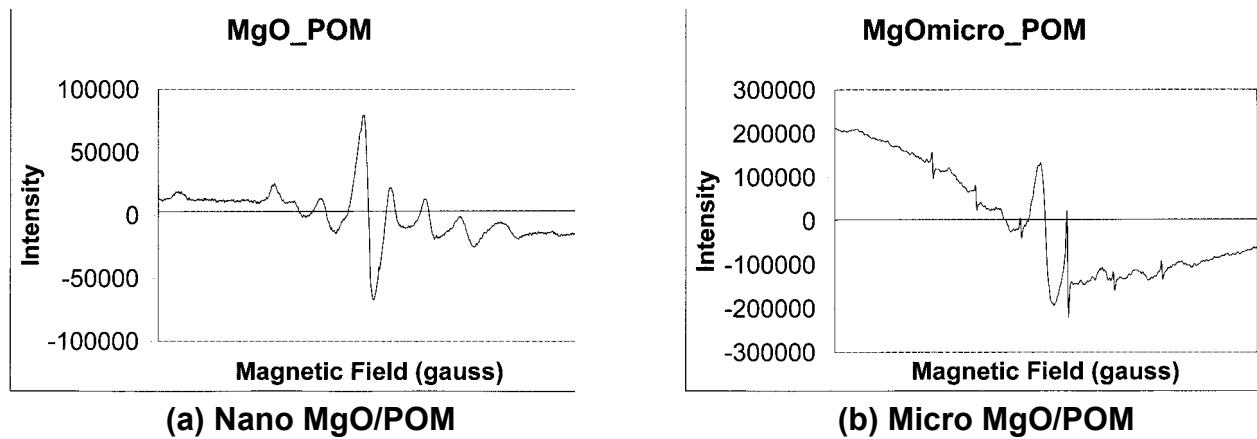


Figure 6. Comparison of ESR spectra for nano MgO/POM and micron MgO/POM.

The ESR spectra of nano MgO/POM exhibits eight widely spaced ESR lines due to the coupling of the unpaired electron in vanadium with the nuclear magnetic moments of the POM atoms and the atoms of magnesium and oxygen in MgO. This spectra is called a powder spectra because of the limited motions (loss of degrees of freedom) of the atoms in the POM adsorbed onto the surface of the nano MgO. In the case of POM adsorbed onto the surface of the micron size MgO particles we can make out the 8 esr lines predicted but superimposed appear to be resonance lines that are of a free spin esr signal which could indicate the a population of POM molecules are not bound to the surface of the metal oxide with the same binding energy as in the nano particle case. Aluminum oxide is another strong oxidizing compound that has been found to significantly decompose half mustard, CEES. Shown in Figure 7 are the reaction rates of POM-treated Al_2O_3 .

REACTION OF CEES WITH POM & POM/ Al_2O_3

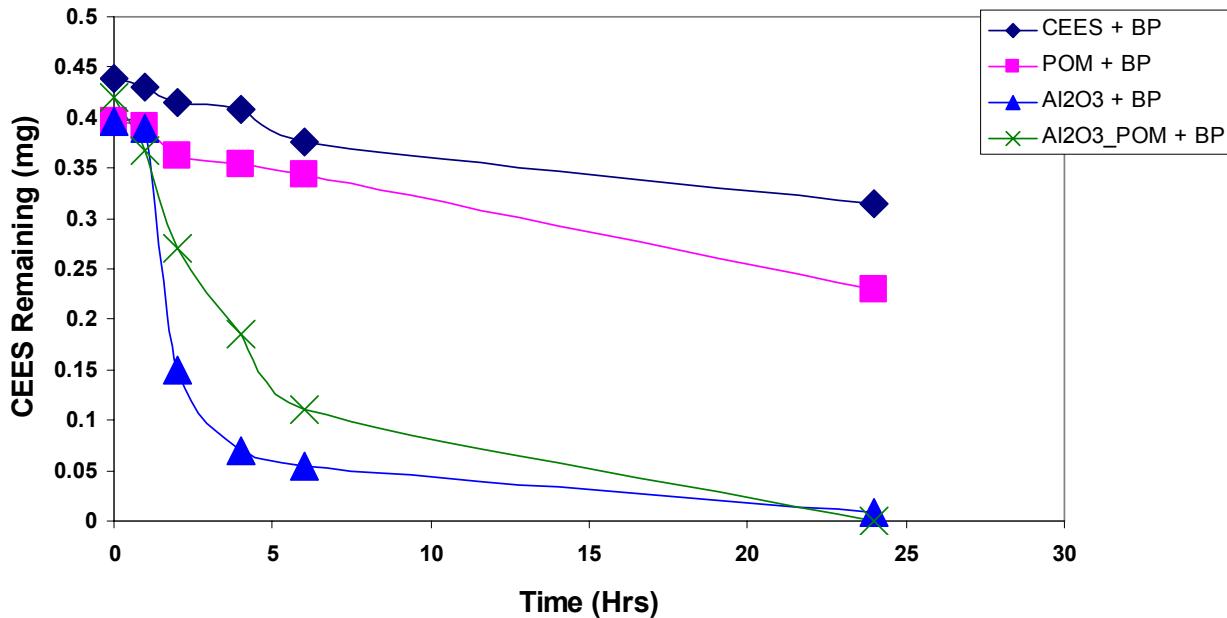


Figure 7. Reaction of nano Al_2O_3 /POM, nano Al_2O_3 with CEES in solution with added BP.

In the reaction of nano $\text{Al}_2\text{O}_3/\text{POM}$ and nano Al_2O_3 with CEES both nano compounds exhibited very nearly the same kinetics for destruction of the CEES. Wagner et al¹³ have shown by solid state NMR that the reaction of nano Al_2O_3 with mustard (HD) occurs by a stoichiometric reaction route in which the products are divinyl sulfide and thiodiglycol. Although the vinyl product can be released partly from the metal oxide, the glycol remains on the surface. As mentioned earlier, POM catalytically transforms thioethers completely to the non-toxic sulfoxide but at this time we cannot predict the exact role of POM in the surface adsorbed aluminum oxide compound. In preliminary studies, we have recently found that POM with aluminum oxide seems to promote a higher ratio of the vinyl product over the glycol, suggesting that more analysis of the POM/ Al_2O_3 compound is warranted.

The effectiveness of the hydrolysis of G-agent surrogate within organic fibers and films for fabric-immobilized catalyst was studied for the catalyst, IBA- β CD. Table 1 shows the rates of hydrolysis of the soman simulant dimebu by IBA- β CD free in solution, encapsulated in both a film and electrospun microfibers of Estane®.

Table 1. Solution Hydrolysis of Dimebu by Free vs. Encapsulated IBA- β CD

Material	Hydrolytic Activity (mmole/min-mg IBA- β CD)
IBA- β CD	2.9
10% IBA- β CD in Electrospun Estane®	1.9
10% IBA- β CD in Estane® Fabric Coating	1.1

In this table, we can see that the reactivity of the encapsulated IBA- β CD in Estane® electrospun microfibers is close to the reactivity of the catalyst free in solution. There is a slight decrease in catalytic hydrolysis when IBA- β CD is incorporated into a film but this may be due to slower diffusion rates for substrate (dimebu) penetration into the thicker membrane, compared to the smaller cross-section fibers.

CONCLUSIONS

Polyoxometalates (POMs) adsorbed on microporous carbons exhibit the best activity for catalytic oxidation of mustard (HD) analogues when compared to POM free in solution, or encapsulated into microfibers or films. POM in microporous carbons doesn't require the co-oxidant, benzoyl peroxide (BP), for optimal catalytic activity.

POMs adsorbed on nano magnesium oxide particles show enhanced reactivity against chloroethyl ethylsulfide (CEES) compared to POM or nano magnesium oxide. This enhanced activity was not observed for the nano aluminum oxide system.

Isodosobenzoate- β -cyclodextrin (IBA- β -CD) was shown to hydrolyze the soman analogue dimebu in solution or encapsulated into electrospun microfibers and films. The reaction rates were diminished slightly by incorporation of the catalyst into the polyurethane fibers and films.

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